Anomalous Diffusion In Microrheology: A Comparative Study

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We present a comparative study on two theoretical descriptions of microrheological experiments. Using a generalized Langevin equation (GLE), we analyze the origin of the power-law behavior of the main properties of a viscoelastic medium. Then, we discuss the equivalence of the GLE with a generalized Fokker-Planck equation (GFPE), and how more general GFPE's can be derived from a thermo-kinetic formalism. These complementary theories lead to a justification for the physical nature of the Hurst exponent of fractional kinetics. Theory is compared with experiments.

I. INTRODUCTION

In the last years, microrheology has become one of the most important experimental techniques in soft condensed matter [1, 2, 3, 4]. It is a powerful technique to determine the viscoelastic properties of complex fluids at time and length scales complementary to those of classical rheological methods [2, 3]. In these complex fluids, ranging from polymer solutions and colloidal suspensions to the intracellular medium, the presence of elastic forces and molecular motors make anomalous the dynamics of the Brownian particles [4, 5, 6]. Hence, anomalous diffusion becomes a central question that must be carefully analyzed due to the presence of confinement and finite-size effects related with particle dimensions. The dynamics of these particles can be described through both, non-Markovian Langevin and Fokker-Planck equations [7, 8, 9, 10, 11]. Here, we use and compare two different formalisms of anomalous diffusion that in the linear force case are equivalent [4].

The article is organized as follows. In Sec. **II** we analyze the generalized Langevin equation and its equivalence with a non-Markovian Fokker-Planck equation. In Sec. **III** we introduce the thermokinetic description, show its equivalence with the GLE formalism in the linear force case, and how it can be generalized to the case of non-linear forces. Sec. **IV** is devoted to the conclusions.

II. THE LANGEVIN APPROACH TO MICRORHEOLOGY

Consider a test Brownian particle of mass m and radius a with position $\mathbf{x}(t)$ and velocity $\mathbf{u}(t) = d\mathbf{x}(t)/dt$. The particle performs its Brownian motion through a viscoelastic medium which can be made up by a solution of polymers or a suspension of particles at sufficiently high concentra-

tion. In these conditions, the motion of the particle could be restricted to a small volume and, consequently, its dynamics may manifest confinement and finite-size effects modifying the anomalous behavior of the mean square displacement (MSD). This last quantity is very important because the viscoelastic properties of the medium can be inferred from it through the Stokes-Einstein relation [4].

In a first approximation, the heat bath can be assimilated as an effective medium that interacts with the particle by means of elastic forces. In first approximation, these forces may be represented through a harmonic force $\mathbf{F}_h = -\omega_m^2 \mathbf{x}$, in which ω_m is a characteristic frequency [4]. Then the dynamics of the particle can be described by means of the generalized Langevin equation

$$\frac{d\mathbf{u}(t)}{dt} = -\omega_m^2 \mathbf{x}(t) - \int_0^\infty \beta(t-\tau)\mathbf{u}(\tau)d\tau + F(t), \quad (1)$$

where $F(t)$ is a random force per unit mass and $\beta(t)$ is a memory function called the friction kernel [7]. In the Markovian case it takes the form: $\beta(t) = \beta_0 \delta(t-\tau)$ with $\beta_0 = 6\pi\eta a/m$ the Stokes friction coefficient per mass unit, η is the viscosity of the solvent and $\delta(t-\tau)$ the Dirac delta function. Hence, in this case Eq. (1) recovers its usual phenomenological form [9].

To describe the diffusion of the particle at sufficiently long times, $t \gg \beta_0^{-1}$, two approximations can be followed.

a) The Overdamped Case. In this case it is assumed that the acceleration term of Eq. (1) can be neglected. As a consequence the GLE takes the approximate form

$$\omega_m^2 \mathbf{x}(t) = -\int_0^\infty \beta(t-\tau)\mathbf{u}(\tau)d\tau + F(t). \quad (2)$$

It is convenient to stress that in Eq. (2), the memory term involves the velocity of the particle.

b) Adiabatic Elimination. In this second approximation, one must first solve Eq. (1) in order to obtain

$$\mathbf{u}(t) = -\omega_m^2 \int_0^\infty \chi(t-\tau)\mathbf{x}(\tau)d\tau + F^*(t), \qquad (3)$$

where we have used Laplace transforms, assumed the initial velocity of the particle as equal to zero for simplicity, and defined the memory function $\chi(t)$ as the inverse Laplace transform $\chi(t) = \mathcal{L}^{-1}\left\{[s+\tilde{\beta}(s)]^{-1}\right\}$. This definition implies that $\chi(t)$ is the relaxation function of the velocity of the particle [7]. Moreover, we have defined the time-scaled random force $F^*(t)$ by

$$F^*(t) = \int_0^\infty \chi(t-\tau)F(t)d\tau. \qquad (4)$$

Using now the identity $\mathbf{u}(t) = d\mathbf{x}(t)/dt = \dot{\mathbf{x}}$, one then obtains the following generalized Langevin equation for the position vector of the particle

$$\dot{\mathbf{x}}(t) = -\omega_m^2 \int_0^\infty \chi(t-\tau)\mathbf{x}(\tau)d\tau + F^*(t). \qquad (5)$$

In the diffusion regime, $t \gg \beta_0^{-1}$, Eqs. (2) and (5) can be considered as the GLE's for the position of the particle and then use them to describe anomalous diffusion of a Brownian particle in a viscoelastic heat bath. They constitute two different models because Eq. (5) differs from (2) in the fact that it can be obtained through an adiabatic elimination of variables, whereas the approximated Eq. (2) has been obtained by neglecting the inertial term. Physically, the difference lies in the fact that the relaxation function of the particle determining the time dependence of the MSD, is different.

Quantitatively, these equations are not simply related one to each other, since the memory kernel and the random force are not equivalent due to the scaling introduced through $\chi(t)$. The fluctuation-dissipation theorem (FDT) associated with Eq. (2) is

$$\langle F(t)F(0)\rangle = \beta(t), \qquad (6)$$

where the bracket $\langle\;\rangle$ means the average over noise realizations. The corresponding FDT for the random force in Eq. (5) is given by the expression $\langle F^*(t)F^*(t')\rangle = \int_0^t d\tau \int_0^{t'} d\tau' \chi(t-\tau)\chi(t'-\tau')\beta(\tau-\tau')$, [9]. However, in the case when the friction kernel is proportional to a Dirac delta function, Eq. (6) defines a thermal (white) noise. After performing the adiabatic elimination of variables, one obtains the relation $\langle F^*(t)F^*(0)\rangle \sim exp(-\beta_0 t)$ for the time-scaled random force. This implies that the position $\mathbf{x}(t)$ of the particles satisfies a non-Markovian equation with a exponentially decaying time correlation of the

random force, [9]. Only in the Markovian case Eqs. (2) and (5) are equal.

At certain time scales, anomalous diffusion is characterized by a power-law behavior of the MSD of the particle as a function of time. Within a Langevin description, this behavior is a consequence of the statistical properties of the random force, that is, of the heat bath as follows from the relations already obtained. In particular, by using Eqs. (2) and (6), it can be shown that anomalous diffusion is a consequence of a fractionary Gaussian noise (FGN) that satisfies the FDT [10]

$$\langle F(t)F(0)\rangle = (k_B T/m)\beta_0^2 2H(2H-1)|\tilde{t}|^{2H-2}, \qquad (7)$$

where the exponent must satisfy the relation: $1/2 \le H \le 1$, the factor β_0^2 gives the correct dimensions and we have introduced the dimensionless time $\tilde{t} = t_0^{-1}t$, with t_0 a characteristic time. In particular, t_0 can be taken as the characteristic diffusion time $\tau_D = a^2 D_0^{-1}$, with $D_0 = k_B T/(m\beta_0)$. Hence, using Eqs. (2) and (7) one may calculate the time dependence of the MSD by using the method of Laplace transforms. Here, it is convenient to write (2) in the dimensionless form

$$\tilde{\mathbf{x}}(\tilde{t}) = -\alpha \int_0^\infty \tilde{\beta}(\tilde{t}-\tilde{\tau})\tilde{\mathbf{u}}(\tilde{\tau})d\tilde{\tau} + \tilde{F}(\tilde{t}). \qquad (8)$$

where $\tilde{\beta}(\tilde{t}) = |\tilde{t}|^{2H-2}$ and $\tilde{F} = a^{-1}\omega_m^{-2}F$ are dimensionless quantities in accordance with Eqs. (7) and (6), and $\alpha = 2H(2H-1)\beta_0^2\omega_m^{-2}$. In writing (8) we have used $\tilde{t}$ and the dimensionless position vector $\tilde{\mathbf{x}} = a^{-1}\mathbf{x}$.

Now, by Laplace transforming Eq. (8), one may obtain the expression for the transformed velocity $\hat{\mathbf{u}}(s)$, which in turn can be substituted into the definition $s\hat{\mathbf{x}}(s) = \hat{\mathbf{u}}(s)$ with $\mathbf{x}(0) = 0$ for simplicity. After solving for $\hat{\mathbf{x}}(s)$ one obtains

$$\hat{\mathbf{x}}(s) = \frac{\alpha^{-1}\Gamma^{-1}(2H-1)s^{2H-2}}{1+\alpha^{-1}\Gamma^{-1}(2H-1)s^{2H-2}}\hat{F}(s). \qquad (9)$$

where $\Gamma(2H-2)s^{1-2H}$ and $\hat{F}(s)$ are the Laplace transforms of $\tilde{\beta}$ and $\tilde{F}$, respectively. The inverse Laplace transform of Eq. (9) is given in terms of the convolution of the noise $\tilde{F}$ and the Mittag-Leffler polynomial $z_*^{1-2H}E_{2-2H,2-2H}\left(-z_*^{2-2H}\right)$, with the scaled variable $z_* = [\alpha\Gamma(2H-1)]^{-1/(2-2H)}\tilde{z}$, [12].

The expression for the MSD can now be obtained by calculating $\langle x^2\rangle(t)$ in terms of the inverse Laplace transform of Eq. (9), using the FDT (7) and performing the corresponding integrals. The general expression involving Mittag-Leffler polynomials is complicated, however at

times t satisfying $\beta_0^{-1} \ll t \sim t_0$, one obtains the following short-time power law behavior

$$\langle x^2 \rangle(t) \sim \left(k_B T \beta_0^2 / m \omega_m^4\right)(t/t_0)^{2-2H}, \qquad (10)$$

where some constants have been dropped for the sake of simplicity.

In Figure **1**, we compare the MSD given by Eq. (10) (dash-dotted lines) with experiments (symbols) of $0.965\mu m$ diameter latex microspheres imbedded in F-actin solutions of increasing concentrations, [3]. As expected, the agreement between theory and experiments is good for short times $\beta_0^{-1} \ll t \sim t_0$ with $t_0 \sim \tau_D$ playing the role of a crossover time. If we take $\beta_0 \sim 10^6 s^{-1}$ then $\tau_D \sim 10^{-2}s$ in typical situations.

The MSD can be used to obtain the microrheological properties of the medium by means of the generalized Stokes-Einstein relation [2]. From Eq. (1) in the zero inertia approximation, one may show that the complex shear modulus of the medium $G''(\omega)$ satisfies the relation

$$G''(\omega) \simeq \left(k_B T / m \omega \langle \hat{x}^2 \rangle(\omega)\right), \qquad (11)$$

where ω is the frequency. Now, by taking the Fourier transform of Eq. (10) and substituting the result into (11), one obtains the scaling relation $G''(\omega) \sim (t_0 \omega)^{2-2H}$. From this analysis it follows that the power-law behavior of the MSD of the particles and the related complex shear modulus of the effective medium, are a consequence of the fractionary Gaussian noise of the GLE (1). Notice that Eq. (5) can also be used to describe anomalous diffusion, however this will be explained after Eq. (15), below.

The Generalized Fokker-Planck Equation. An equivalent approach to study anomalous diffusion in a viscoelastic bath can be performed by means of a generalized Fokker-Planck equation .

By using the Laplace transform technique, in Ref. [7] it has been shown that the GLE (1) is equivalent to the following non-Markovian Fokker-Planck equation containing time dependent coefficients

$$\frac{\partial}{\partial t} f + \frac{\partial}{\partial \mathbf{x}} \cdot (\mathbf{u} f) - \tilde{\omega}^2(t)\mathbf{x} \cdot \frac{\partial f}{\partial \mathbf{u}} = \psi(t)\frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial f}{\partial \mathbf{x}}$$
$$+ \frac{\partial}{\partial \mathbf{u}} \cdot \tilde{\beta}(t)\left[\mathbf{u} f + \frac{k_B T}{m}\frac{\partial f}{\partial \mathbf{u}}\right]. \quad (12)$$

Here, $f(\mathbf{x}, \mathbf{x}_0; \mathbf{u}, \mathbf{u}_0, t)$ is the probability distribution function depending on the instantaneous position $\mathbf{r}$ and velocity $\mathbf{u}$ of the Brownian particle. $\mathbf{r}_0$ and $\mathbf{u}_0$ are the corresponding initial conditions. In this equation, memory effects are incorporated through the time dependent coefficients $\tilde{\beta}(t)$ and $\tilde{\omega}(t)$ and $\psi(t) =$
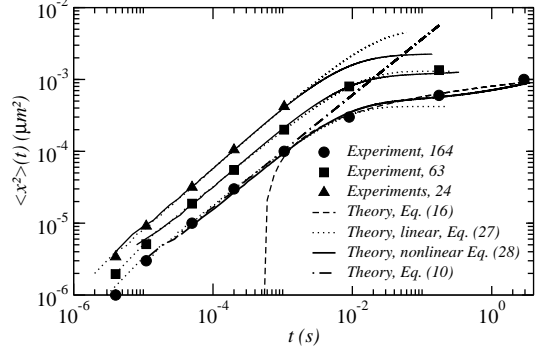

FIG. 1: MSD vrs time. Comparison between theory (lines) and experiments with actin filament networks (symbols) (taken from Ref. [3]). The dashed line corresponds to the power law behavior valid for long times, Eq. (16) with $t_0 = 2 \cdot 10^{-3}s$, $\omega_m \sim 2.6 \cdot 10^2 s^{-1}$, and $b \sim 1 \cdot 10^{-2}$. The dotted lines correspond to a stretched exponential behavior Eq. (27), with $\omega_T^2/\omega_m^2 \sim 5.61 \cdot 10^{-4}$, $2\omega_m^2 B_2 t_0 / \alpha \beta_0 \sim 35$ and $2\beta_0/\alpha t_0 \omega_m^2 = 3/4$. The solid lines correspond to the nonlinear model Eq. (28). The values of the parameters are indicated in the text. The dash-dotted line corresponds to Eq. (10) with $H = 5/8$. The numbers 24, 63 and 124 correspond to increasing concentrations of actin filaments, [3].

$(k_B T / m \omega_m^2)\left[\tilde{\omega}^2(t) - \omega_m^2\right]$. They are given in terms of combinations of the relaxation functions $\chi_u(t) = m(3k_B T)^{-1}\langle \mathbf{x}(t) \cdot \mathbf{u}_0 \rangle$ and $\chi_x(t) = \langle \mathbf{x}_0^2 \rangle^{-1}\langle \mathbf{x}(t) \cdot \mathbf{x}_0 \rangle$, and their explicit form is given in Ref. [7]. It is worth to stress here that an equation similar to (12) has also been obtained by using projector operator techniques in [8].

The result expressed in Eq. (12) is important, because it implies that generalized Fokker-Planck equations incorporating memory effects through memory functions constitute models not simply related with Eq. (1), [1, 4]. Passing from one model to the other implies an approximation that imposes conditions on the rate of change of the fields involved in the description [4, 9, 11].

At times $t \gg \beta_0^{-1}$, from Eq. (12) one may derive a generalized Smoluchowski equation for the mass density $\rho(\mathbf{x}, t) = m \int f d\mathbf{u}$. To derive it, one may follow the adiabatic elimination of variables procedure by calculating the evolution equations for the first three moments of $f(\mathbf{x}, \mathbf{u}, t)$. Then, after imposing the condition of large times $t \gg \beta_0^{-1}$, a reduced description is obtained in terms of an evolution equation for ρ.

Averaging Eq. (12) over $\mathbf{u}$ assuming that the currents vanish at the boundaries, we obtain the continuity equation

$$\partial \rho / \partial t = -\nabla \cdot (\rho \mathbf{v}), \qquad (13)$$

where $\mathbf{v}(\mathbf{x}, t) = m\rho^{-1} \int \mathbf{u} f d\mathbf{u}$ is the average velocity field. At long times one obtains the following constitutive relation for the diffusion current [13]

$$\rho\mathbf{v} \simeq -\tilde{\beta}^{-1}\tilde{\omega}^2\mathbf{x}\rho - \tilde{D}\nabla\rho, \qquad (14)$$

where we have defined the effective diffusion coefficient $\tilde{D}(t) = (k_B T/m\omega_m^2)\tilde{\beta}^{-1}\tilde{\omega}^2$ and used the definition of $\psi(t)$. Substitution of Eq. (14) into (13) leads to

$$\partial\rho/\partial t = \tilde{D}(t)\left[\nabla^2\rho - \left(m\omega_m^2/k_B T\right)\nabla\cdot(\rho\mathbf{x})\right], \qquad (15)$$

which constitutes the generalized Smoluchowski equation (GSE) for ρ. An equation similar to (15) can also be obtained from Eq. (1) by using Laplace transforms. In Ref. [14], the authors found that $(m/k_B T)\tilde{D}(t)$ is proportional to $-d\ln|R(t)|/dt$, with $R(t) = \chi(t)/\chi(t_0)$ and $\chi(t) = \langle\mathbf{x}\cdot\mathbf{x}_0\rangle(t)$ the relaxation function of the position of the particle. If one considers the case of FGN, the relaxation function $R(t)$ is given in terms of a Mittag-Leffler polynomial leading to a complicated form for the effective diffusion coefficient $\tilde{D}(t)$, [10]. By evaluating numerically the obtained relation, it can be shown that at short times the function follows a power law behavior with an exponent equal to that calculated by simply taking the time derivative of Eq. (10). At larger times, a crossover arises in which the relaxation function can be assumed to decay as the power law $R(\tilde{t}) \sim \tilde{t}^{-b}$. Using the definition $\langle x^2\rangle = \int x^2\rho\, d\mathbf{x}$, Eq. (15) and assuming $\tilde{\beta}^{-1}\tilde{\omega}^2 = \beta_0^{-1}\omega_m^2\tilde{\gamma}(\tilde{t})$, with $\tilde{\gamma}$ dimensionless, one may calculate the following expression for the MSD

$$\langle x^2\rangle \sim 3(k_B T/m\omega_m^2)\left[1 - (t/t_0)^{-2b}\right]. \qquad (16)$$

At times $t \gg t_0$, Eq. (16) can be used to fit the experimental results, as shown by the dashed line in Figure **1**. See the discussion after Eq. (10).

This analysis shows that, in the linear force case the GLE with FGN offers a good explanation of the subdiffusion observed in microrheological experiments. A different approach in order to have deeper understanding of the physical mechanisms responsible for subdiffusion in a viscoelastic fluid will be presented in the following section.

III. THERMOKINETIC-DESCRIPTION OF ANOMALOUS DIFFUSION

The Fokker-Planck type Eqs. (12) and (15) for the probability distribution function, admit a different interpretation in terms of kinetic equations. This reinterpretation enriches and simplifies the description of anomalous diffusion, because allows one to formulate phenomenological

models for the coefficients $\tilde{\beta}$ and $\tilde{\omega}$ which not do depend on the *a priori* election of the statistical properties of the random force of Eq. (1).

Fokker-Planck type kinetic equations for different physical phenomena can be obtained by using two general principles. The first one is the conservation of the probability, expressed by the equation

$$\partial f(\underline{\Gamma}, t)/\partial t = -\nabla_\Gamma \cdot [f(\underline{\Gamma}, t)\mathbf{V}_\gamma], \qquad (17)$$

where $\underline{\Gamma}$ represents the set of variables necessary to describe the state of the system at a mesoscopic level. Here, $f(\underline{\Gamma}, t)\mathbf{V}_\gamma$ represents a diffusion current in $\underline{\Gamma}$-space and ∇_Γ the corresponding gradient operator. The second principle is the so-called generalized Gibbs entropy postulate [6, 15]

$$\rho\Delta s(t) = -k_B \int f(\underline{\Gamma}, t)\ln|f(\underline{\Gamma}, t)/f_{leq}(\underline{\Gamma})|\, d\underline{\Gamma}, \qquad (18)$$

where Δs is the difference of the specific entropy with respect to a local equilibrium reference state, characterized through the probability distribution $f_{leq}(\underline{\Gamma})$. The assumption of local equilibrium allows one to calculate $f_{leq}(\underline{\Gamma})$ by using the techniques of equilibrium statistical mechanics.

To obtain the evolution equation for $f(\underline{\Gamma}, t)$, we may follow the rules of mesoscopic nonequilibrium thermodynamics (MNET) [6, 16]. Schematically, by taking the time derivative of Eq. (18) and inserting (17), after integrating by parts assuming the usual boundary conditions, one obtains the entropy production $\sigma(t)$

$$\sigma(t) = -\frac{m}{T}\int f(\underline{\Gamma}, t)\mathbf{V}_\gamma \cdot \nabla_\Gamma\left[\frac{k_B T}{m}\ln|f/f_{leq}|\right] d\underline{\Gamma}. \quad (19)$$

In a similar way as in linear irreversible thermodynamics [15], we can assume linear relationships between the forces $(k_B T/m)\ln|f/f_{leq}(\underline{\Gamma})|$ and the conjugated currents $f\mathbf{V}_\gamma$. Using them, one finally arrives at the multivariate Fokker-Planck equation

$$\partial f/\partial t = \nabla_\Gamma \cdot \underline{\tilde{\xi}}(t)\left[(k_B T/m)\nabla_\Gamma f - (f\mathbf{X})\right], \qquad (20)$$

where the generalized force $\mathbf{X}(\underline{\Gamma})$ is defined in the usual form: $\mathbf{X} = -k_B T\nabla_\Gamma\ln f_{leq}$, [9]. Here, memory effects are incorporated through the time dependent Onsager coefficients introduced by the linear coupling between forces and fluxes, and contained in $\underline{\tilde{\xi}}(t)$, [4, 13]. The tensorial character of $\underline{\tilde{\xi}}(t)$ accounts for the anisotropy of the medium.

If we consider a Brownian particle under the action of a linear force and whose mesoscopic state is determined

by its instantaneous velocity $\mathbf{u}$ and position $\mathbf{x}$, Eq. (20) takes the form (12). In this case, the local equilibrium distribution is $f_{leq} = f_0 exp\left[-(k_B T/2m)\left(\mathbf{u}^2 + 2\phi\right)\right]$, where $\phi(\mathbf{x})$ is the potential associated with the harmonic force, f_0 is a normalization factor and we have assumed that in Γ-space entropic forces are coupled to the currents independently from those arising from an energy potential, reflecting its different physical origin [13].

At larger times, we may assume that the state of the particle is only determined by its position vector, then the local equilibrium distribution is $\rho_{leq} = \rho_0 exp\left[-(k_B T/m)\phi(\mathbf{x})\right]$, where the potential $\phi(\mathbf{x})$ is arbitrary. By following the procedure indicated above, the following GSE can be derived

$$\partial\rho/\partial t = D(t)\left\{\nabla^2\rho - (m/k_B T)\nabla\cdot[\rho\mathbf{X}(\mathbf{x})]\right\}, \quad (21)$$

where we have assumed an isotropic medium when writing the scalar effective diffusion coefficient $D(t)$ and defined $\mathbf{X} = -\nabla\phi(\mathbf{x})$. Hence, the thermokinetic formalism allows one to derive generalized Fokker-Planck equations of the form (21) which contain nonlinear forces. No assumptions on the statistical nature of the random force have been done until now. This is an important difference with respect to the GLE description, because the method presented in the second section gives exact Fokker-Planck equations only in the case of linear forces.

During its motion through the viscoelastic medium, the Brownian particle induces perturbations on the velocity field of the host fluid surrounding it. These perturbations propagate and are reflected by the local boundaries which can be made up by a polymer network or another suspended particles. As a consequence, they modify the velocity field of the fluid around the particle in a later time, introducing memory effects. In this form, hydrodynamic interactions change the distribution of stresses used to calculate the force over the surface of the particle. In first approximation, this force is characterized by the effective mobility coefficient $\gamma(t) = (m/k_B T)D(t)$, in the form [4]

$$\gamma(t) = \beta_0^{-1}\alpha\tilde{\gamma}(t). \quad (22)$$

Here, $\tilde{\gamma}(t)$ is a dimensionless function of time and $\alpha = 1 + B_1 a/y$ is the mentioned correction [4, 17, 18]. The coefficient B_1 depends on the nature of the boundary (solid wall, membrane, polymer network or a cage formed by surrounding particles) and y represents a characteristic length of the medium.

By using the dimensionless variables previously introduced and defining the time scaling $\tau(t) = \int\tilde{\gamma}(t)dt$, from
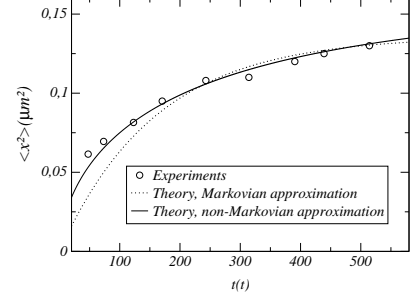

FIG. 2: MSD vrs time. Comparison between theory (lines) and experiments of chromatin diffusion in living cells. The dotted line corresponds to a linear model in the Markovian approximation. The data were taken from Ref. [5] (circles) and the figure from [20].

(21) one obtains

$$\partial\rho/\partial\tau = \alpha\left(\omega_T^2 t_0/\beta_0\right)\tilde{\nabla}^2\rho - \alpha\left(F_0 t_0/\beta_0 a\right)\tilde{\nabla}\cdot\left(\rho\tilde{\mathbf{X}}\right), \quad (23)$$

where $\omega_T^2 \equiv k_B T/ma^2$ and F_0 is the magnitude of the force per unit mass $\mathbf{X}$ due, for instance, to the polymer network.

The time dependence of τ can be obtained by using the evolution equation for the time correlation function $\chi(\tilde{t}) = \langle\tilde{\mathbf{x}}\cdot\tilde{\mathbf{x}}_0\rangle(\tilde{t})$ (see, Eq. 15), [4]

$$d\chi(\tilde{t})/d\tilde{t} = -\alpha\left(F_0 t_0/\beta_0 a\right)\tilde{\gamma}(\tilde{t})\langle\tilde{\mathbf{X}}\cdot\tilde{\mathbf{x}}_0\rangle(\tilde{t}). \quad (24)$$

Eq. (24) involves a complete hierarchy for the moments of the distribution ρ. However, in the linear force case it takes a closed form leading to the relation

$$\gamma(\tilde{t}) = d\ln\left|R^{-\beta_0/\alpha t_0\omega_m^2}\right|/d\tilde{t}, \quad (25)$$

where we have used $\mathbf{X} = -\omega_m^2\mathbf{x}$ with $\omega_m^2 = a^{-1}F_0$ and $R(\tilde{t}) = \chi(\tilde{t})/\chi(0)$. Using the definition and Eq. (25) one gets $\tau(\tilde{t}) = \ln\left|R^{-\beta_0/\alpha t_0\omega_m^2}\right|$. These relations imply: $D = \tilde{D}$, see the discussion after Eq. (15).

At short times, we can infer the time dependence of $\tau(\tilde{t})$. Expanding the logarithm in its argument around the unity: $\ln|R^{-\beta_0/\alpha t_0\omega_m^2}| \simeq R^{-\beta_0/\alpha t_0\omega_m^2} - 1 + O(R^2)$ and taking into account that $R(\tilde{t})$ must be an even function of time, a first order expansion leads to: $R^{-1}(\tilde{t}) \simeq 1 + B_2^*\tilde{t}^2 + O(\tilde{t}^4)$. Thus, we obtain the approximate expression

$$\tau(\tilde{t}) \sim B_2\tilde{t}^{2\beta_0/\alpha t_0\omega_m^2}, \quad (26)$$

where the parameter $B_2 \propto B_2^*$ in general depends on the characteristic length of the medium [4]. Important to
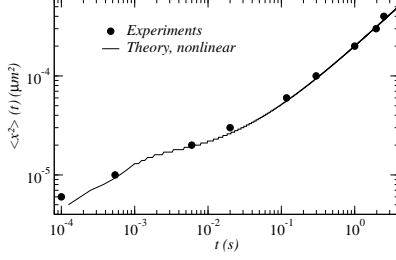
FIG. 3: MSD vrs time. Comparison between experiments (circles) and theory (solid line) for the case of actin filament networks. The data were taken from Ref. [3]. The theoretical model corresponds to Eq. (28) with $\langle x^2 \rangle_0 \sim 4.4 \cdot 10^{-6} \mu m^2$, $D_0 \sim 9.3 \cdot 10^{-5} \mu m^2 s^{-1}$, $\beta_0 \sim 5.5 \cdot 10^9 s^{-1}$, $F_0 \sim 3.8 \cdot 10^{-4} \mu m\, s^{-2}$, $t_0 \sim 0.1s$, $\lambda \sim 1.5 \cdot 10^{-3} \mu m$, $B_2 \sim 60$, $\alpha \sim 1$.

notice is that the exponent depends on β_0, t_0, ω_m and α. Eq. (26) is consistent with a stretched exponential relaxation of the correlations [19]. Hence, in the linear case, Eq. (23) gives the MSD

$$\langle \tilde{x}^2 \rangle(\tau) = 3(\omega_T^2/\omega_m^2) \left[1 - e^{-2\alpha\omega_m^2 t_0 \tau(t)/\beta_0} \right], \qquad (27)$$

which at short times yields $\langle \tilde{x}^2 \rangle \simeq 6 B_2 \frac{\alpha \omega_T^2}{\beta_0 t_0^{-1}} \tilde{t}^{2\beta_0/\alpha t_0 \omega_m^2}$. Comparison with Eq. (10) leads to the identifications $t_0 \sim \beta_0^3 \omega_m^{-4}$ and $H = 1 - \beta_0/\alpha t_0 \omega_m^2$. This expression for H constitutes the central result of this work. It shows that the so-called Hurst exponent is a consequence of hydrodynamic and elastic interactions between the particle and the viscoelastic medium.

This model explains the behavior of the MSD in the case of constrained diffusion [4]. Fig. **2** shows a comparison between theory (solid line) and experiments of constrained diffusion of chromatin in living cells [5]. The dashed line corresponds to a similar model in the Markovian case. As expected, the short time behavior of the MSD is subdiffusive. These effects are also present in Fig. **1** (dotted lines). At short times the behavior of MSD follows a power law on the scaled time $\tilde{t}$ and saturates at long times, where confinement becomes significant. A more detailed model is reported in [4].

A nonlinear model can also be discussed in terms of Eq. (21). If we assume that the force exerted on the particle by the medium is of the form $\cos\left[\lambda^{-1}\langle x\rangle(\tau)\right]$, with λ the average distance between the particle and the local boundaries, it can be shown that [4]

$$\langle x^2 \rangle(t) \simeq \langle x^2 \rangle_0 + 2D_0 \tau(t) + 4\lambda^2 \tanh\left[\frac{F_0 D_0}{2\lambda k_B T}\tau(t)\right]^2, \qquad (28)$$

where $\langle x^2 \rangle_0$ is some initial value. The behavior of the MSD (28) as a function of time (solid line) is shown in Figs. **1** and **3**, and compared with experiments (symbols). The plateau is a signature of the existence of cage effects, which in our model are related with the maximum value of the elastic force **X**. The agreement between theory and experiments is good.

For Fig. **1** in the case with label 164, the values of the parameters are: $\langle x^2 \rangle_0 \sim 5 \cdot 10^{-7} \mu m^2$, $D_0 \sim 1.3 \cdot 10^{-4} \mu m^2 s^{-1}$, $\beta_0 \sim 5.5 \cdot 10^9 s^{-1}$, $F_0 \sim 1 \cdot 10^{-3} \mu m\, s^{-2}$, $t_0 \sim 0.1s$, $\lambda \sim 1.1 \cdot 10^{-2} \mu m$, $B_2 \sim 7.2$, $\alpha \sim 1$ and we have defined $\omega_m^2 \sim F_0 \lambda^{-1}$. Finally, it is interesting to notice that the effective mobility $\gamma(t)$ may be interpreted phenomenologically as the inverse Laplace transform: $\mathcal{L}^{-1}\left[\omega/G''(\omega)\right]$. Taking into account the relation between the MSD and the compliance J: $\langle x^2 \rangle(t) \sim J(t)$, [3], one obtains $\gamma(t) = \mathcal{L}^{-1}\left[\omega^2 J(\omega)\right]$.

IV. CONCLUSIONS

By following two different approaches, in this article we have described the anomalous diffusion of a Brownian particle in microrheological experiments. In the linear force case, we have shown that the generalized Langevin description with fractionary Gaussian noise explains well the behavior of the microrheological properties of the viscoelastic medium. We have also shown the equivalence of this description with generalized Fokker-Planck equations having time dependent coefficients. The comparison with a thermokinetic formalism gives a plausible justification for the physical nature of the exponent $H = 1 - \beta_0/\alpha t_0 \omega_m^2$ used in the GLE description. The thermokinetic formalism constitutes a powerful generalization of the theory allowing the formulation of non-Markovian models even in the case of non-linear forces. The agreement between theory and experiment is good.

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